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(54) Title: SURFACE-ACTIVE FORMULATIONS			
(57) Abstract  The invention relates to surface-active soap formulations, comprising: (a) 0.01 to 5 % by weight of a microbicidal active substance selected from the group consisting of (a <sub>1</sub> ) phenol derivatives (a <sub>2</sub> ) diphenyl compounds (a <sub>3</sub> ) benzyl alcohols (a <sub>4</sub> ) chlorohexidine (a <sub>5</sub> ) C <sub>12</sub> -C <sub>14</sub> alkylbetaines and C <sub>8</sub> -C <sub>18</sub> fatty acid amidoalkylbetaines (a <sub>6</sub> ) amphoteric surfactants and (a <sub>7</sub> ) trihalocarbanilides; (b) 0.1 to 25 % by weight of one or more than one hydrotropic agent; (c) 0 to 10 % by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances; (d) 0 to 8 % by weight of a salt of a saturated and/or unsaturated C <sub>8</sub> -C <sub>22</sub> fatty acid; (e) 0 to 50 % by weight of a dihydric alcohol; (f) 0 to 70 % by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and (g) mains water or deionised water to make up 100 %, with the proviso that the formulations contain at least one of components (c) and (d). The formulations are used for the disinfection and cleansing of the human skin and hands and of hard objects.			

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### Surface-active formulations

It is commonly knowledge that the antimicrobial/microbicidal properties of active substances in aqueous solutions of soaps or surfactants are strongly influenced by micell systems and may even be almost totally blocked.

Surprisingly, it has now been found that certain hydrotropic suppress the microbicidal inhibiting activity of the micells of soap and surfactant systems (so-called "deblocked surfactant systems"). Accordingly, the antimicrobial/microbicidal activity of different active ingredients can be significantly enhanced in many surfactant systems.

The novel surface-active surfactant formulations comprise

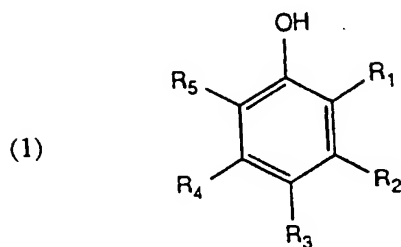
- (a) 0.01 to 5% by weight of a microbicidal active substance selected from the group consisting of
    - (a<sub>1</sub>) phenol derivatives,
    - (a<sub>2</sub>) diphenyl compounds,
    - (a<sub>3</sub>) benzyl alcohols,
    - (a<sub>4</sub>) chlorohexidine,
    - (a<sub>5</sub>) C<sub>12</sub>-C<sub>14</sub>alkylbetaines and C<sub>8</sub>-C<sub>18</sub>fatty acid amidoalkylbetaines,
    - (a<sub>6</sub>) amphoteric surfactants,
    - (a<sub>7</sub>) trihalocarbanilides, and
    - (a<sub>8</sub>) quaternary ammonium salts;
  - (b) 0.1 to 25% by weight of one or more than one hydrotropic agent;
  - (c) 0 to 10% by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances;
  - (d) 0 to 8% by weight of a salt of a saturated and/or unsaturated C<sub>8</sub>-C<sub>22</sub>fatty acid;
  - (e) 0 to 50% by weight of a dihydric alcohol;
  - (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
  - (g) mains water or deionised water to make up 100%,
- with the proviso that the formulations contain at least one of components (c) and (d).

Soap formulations will be understood as meaning aqueous soap solutions which may be obtained as soap or so-called syndet solutions (= synthetic detergents).

The antimicrobial activity of the deblocked surfactant systems reaches upon gram-positive

and gram-negative bacteria as well as yeasts, dermatophytes and the like.

The compounds of component (a<sub>1</sub>) preferably correspond to the general formula



wherein

R<sub>1</sub> is hydrogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkyl, chloro, nitro, phenyl oder benzyl,

R<sub>2</sub> is hydrogen, hydroxy, C<sub>1</sub>-C<sub>6</sub>alkyl or halogen,

R<sub>3</sub> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,

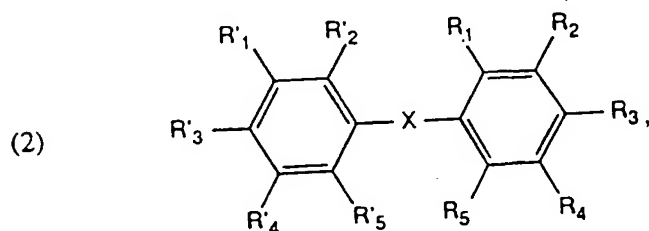
R<sub>4</sub> is hydrogen or methyl,

R<sub>5</sub> is hydrogen or nitro.

Halogen is bromo or, preferably, chloro.

Such compounds are typically chlorophenols (o-, m-, p-chlorophenols), 2,4-dichlorophenol, p-nitrophenol, picric acid, xylenol, p-chloro-m-xyleneol, cresols (o-, m-, p-cresols), p-chloro-m-cresol, pyrocatechin, resorcinol, orcinol, 4-n-hexylresorcinol, pyrogallol, phloroglucine, carvacrol, thymol, p-chlorothymol, o-phenylphenol, o-benzylphenol, p-chloro-o-benzylphenol and 4-phenolsulfonic acid.

The compounds of component (a<sub>2</sub>) preferably correspond to the general formula



wherein

X is sulfur or the methylene group,

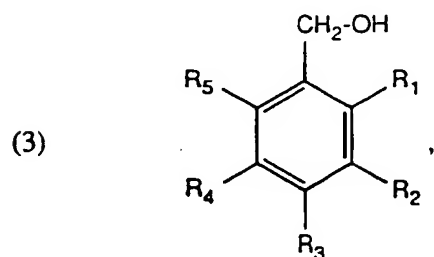
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$R_1$  and  $R'_1$  are hydroxy, and

$R_2, R'_2, R_3, R'_3, R_4, R'_4, R_5$  and  $R'_5$  are each independently of one another hydrogen or halogen.

Typical examples of compounds of formula (2) are hexachlorophene, tetrachlorophene, dichlorophene, 2,3-dihydroxy-5,5'-dichlorodiphenylsulfide, 2,2'-dihydroxy-3,3',5,5'-tetrachlorodiphenylsulfide, 2,2'-dihydroxy-3,3',5,5',6,6'-hexachlorodiphenylsulfide and 3,3'-dibromo-5,5'-dichloro-2,2'-dihydroxydiphenylamine.

The compounds of component ( $a_3$ ) preferably correspond to the general formula



wherein

$R_1, R_2, R_3, R_4$  and  $R_5$  are each independently of one another hydrogen or chloro.

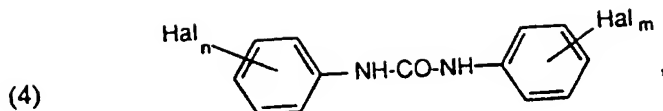
Illustrative examples of compounds of formula (3) are benzyl alcohol, 2,4-, 3,5- or 2,6-dichlorobenzyl alcohol and trichlorobenzyl alcohol.

Component ( $a_4$ ) is chlorohexidine and salts thereof together with organic and inorganic acids, which type of compound may preferably be incorporated into syndet systems.

Component ( $a_5$ ) is typically  $C_8$ - $C_{18}$ cocamidopropylbetaine.

Amphoteric surfactants corresponding to component ( $a_6$ ) are suitably  $C_{12}$ alkylaminocarboxylic and  $C_1$ - $C_3$ alkanecarboxylic acids such as alkylaminoacetates or alkylaminopropionates.

The compounds of component ( $a_7$ ) preferably correspond to the general formula



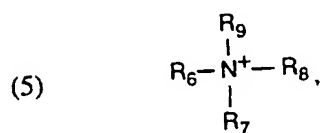
wherein

Hal is chloro or bromo,

n and m are 1 or 2, and

n + m are 3.

The quaternary ammonium salts of component (a<sub>8</sub>) preferably correspond to formula

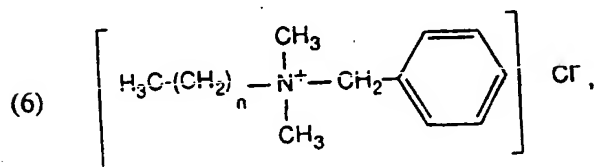


wherein

R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are each independently of one another C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>1</sub>-C<sub>18</sub>alkoxy or phenyl-lower alkyl, and

Hal is chloro or bromo.

Among these salts, the compound of formula



wherein

n is an integer from 7 to 17, is very particularly preferred.

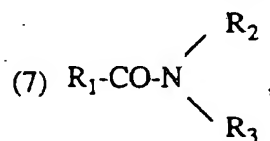
The following compounds are suitable for use as component (b):

(b<sub>1</sub>): sulfonates, preferably the salts thereof of terpenoids, or mono- or binuclear aromatic compounds, typically sulfonates of camphor, toluene, xylene, cumene or naphthene;

(b<sub>2</sub>): saturated or unsaturated C<sub>3</sub>-C<sub>12</sub>di- or polycarboxylic acids, typically malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, undecanedicarboxylic acid and dodecanedicarboxylic acid, fumaric, maleic, tartaric

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- and malic acid as well as citric and aconitic acid;
- (b<sub>3</sub>):
- aliphatic saturated or unsaturated C<sub>1</sub>-C<sub>11</sub> monocarboxylic acids, typically acetic, propionic, hexanoic, capric or undecylenoic acid;
  - saturated or unsaturated C<sub>3</sub>-C<sub>12</sub> di- or polycarboxylic acids, typically malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acid, undecanecarboxylic and dodecanedicarboxylic acid, fumaric, maleic, tartaric and malic acid as well as citric and aconitic acid;
  - aminocarboxylic acids, typically ethylenediaminetetracetic acid, hydroxyethyl-ethylenediaminetetracetic acid and nitrilotriacetic acid;
  - cycloaliphatic carboxylic acids such as camphoric acid;
  - aromatic carboxylic acids, typically benzyl, phenylacetic, phenoxyacetic and cinnamic acid, 2-, 3- and 4-hydroxybenzoic acid, anilinic acid as well as o-, m- and p-chlorophenylacetic acid and o-, m- and p-chlorophenoxyacetic acid;
  - alkali metal salts and amine salts of inorganic acids, typically the sodium or potassium salts and amine(R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) salts of hydrochloric, sulfuric, phosphoric, C<sub>1</sub>-C<sub>10</sub>alkylphosphoric acid and boric acid, in which amine salts R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> have the meaning indicated above;
  - isethionic acid;
  - tannic acid;
  - acid amides of formula



wherein

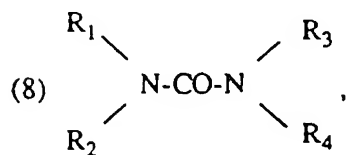
R<sub>1</sub> is hydrogen or C<sub>1</sub>-C<sub>12</sub>alkyl, and

R<sub>2</sub> and R<sub>3</sub> are each independently of the other hydrogen, C<sub>1</sub>-C<sub>12</sub>alkyl,

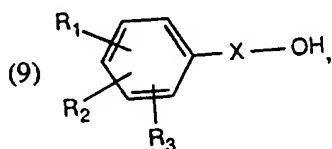
C<sub>2</sub>-C<sub>12</sub>alkenyl, C<sub>1</sub>-C<sub>12</sub>hydroxyalkenyl, C<sub>2</sub>-C<sub>12</sub>hydroxyalkyl, or a polyglycol ether chain containing 1 to 30 -CH<sub>2</sub>-CH<sub>2</sub>-O- or -CHY<sub>1</sub>-CHY<sub>2</sub>-O- groups, wherein

Y<sub>1</sub> or Y<sub>2</sub> is a hydrogen radical and the other is methyl, e.g. N-methylacetamide;

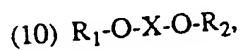
- urea derivatives of formula



wherein  
 $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently of one another hydrogen,  $C_1$ - $C_8$ alkyl,  
 $C_2$ - $C_8$ alkenyl,  $C_1$ - $C_8$ hydroxyalkyl or  $C_2$ - $C_8$ hydroxyalkenyl;  
 - monohydric  $C_4$ - $C_{18}$ aliphatic and monocyclic alcohols, typically  $C_2$ - $C_{18}$ alkanols,  
 $C_2$ - $C_{18}$ alkenols and terpene alcohols e.g. ethanol, propanol, isopropanol, hexanol,  
 cis-3-hexen-1-ol, trans-2-hexen-1-ol, 1-octen-3-ol, heptanol, octanol,  
 trans-2-cis-6-nonadien-1-ol, decanol, linalol, geraniol, dihydroterpineol,  
 myrcenol, nopol and terpineol;  
 - aromatic alcohols of formula



wherein  
 $X$  is  $-(CH_2)_{1-6}$ ,  $-CH=CH-CH_2-$ , or  $-O-(CH_2)_{2-6}$ , and  
 $R_1$ ,  $R_2$  and  $R_3$  are each independently of one another hydrogen, hydroxy, halogen  
 or  $C_1$ - $C_6$ alkoxy, typically benzyl alcohol, 2,4-dichlorobenzyl alcohol,  
 phenoxyethanol, 1-phenoxy-2-propanol (phenoxyisopropanol) and cinnamyl  
 alcohol;  
 - polyhydric alcohols and polyhydric alkoxyated, preferably ethoxylated and/or  
 propoxylated alcohols as well as the ethers and esters thereof of the general  
 formula



wherein  
 $R_1$  and  $R_2$  are each independently of the other hydrogen,  $C_1$ - $C_{12}$ alkyl,  
 $C_2$ - $C_{12}$ alkenyl,  $C_1$ - $C_8$ alkanoyl,  $C_3$ - $C_{18}$ alkenoyl,  
 $R_3-(OCH-CH_2)_{1-50}$ , wherein

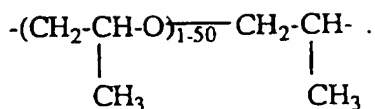


$R_3$  is hydrogen,  $C_1$ - $C_{12}$ alkyl or  $C_2$ - $C_{12}$ alkenyl, and  
 $R_4$  is hydrogen or  $-CH_3$ , and

$X$  is  $C_2$ - $C_{10}$ alkylene or  $C_2$ - $C_{10}$ alkenylene,  $-(CH_2CH_2O)_{1-50}CH_2-CH_2-$  or



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All organic acids mentioned under (b) may also be obtained in the form of their water-soluble salts, such as the alkali metal salts, preferably the sodium or potassium salts or the amine(NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) salts, wherein

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently of one another hydrogen,

C<sub>1</sub>-C<sub>8</sub>alkyl, C<sub>2</sub>-C<sub>8</sub>alkenyl, C<sub>1</sub>-C<sub>8</sub>hydroxyalkyl, C<sub>5</sub>-C<sub>8</sub>cycloalkyl or polyalkenylenoxy-C<sub>1</sub>-C<sub>18</sub>alkyl, or

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, together with the linking nitrogen atom, are unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl-substituted morpholino.

Component (b) can consist of only one compound of subclass (b<sub>1</sub>) or also of mixtures of one or more than one compound of subclass (b<sub>1</sub>), also together with components of further subclasses.

A special antimicrobial activity is achieved with a combination of one or more than one compound of subclass (b<sub>1</sub>) and one or more than one compound of subclass b<sub>2</sub>).

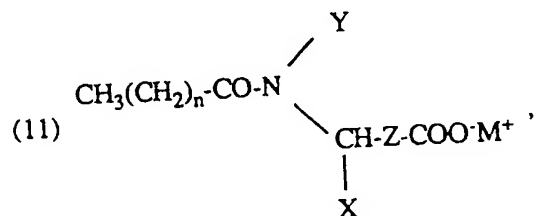
Particularly preferred in this connection is a combination of cumene sulfonate and citric acid monohydrate.

Suitable components (c) are anionic, nonionic or zwitterionic and amphoteric synthetic, surface-active substances.

Suitable anionic surface-active substances are:

- sulfates, typically fatty alcohol sulfates, which contain 8 to 18 carbon atoms in the alkyl chain, e.g. sulfated lauryl alcohol;
- C<sub>8</sub>-C<sub>22</sub>fatty alcohol ether sulfates, typically the acid esters or the salts thereof of a polyadduct of 2 to 30 mol of ethylene oxide with 1 mol of a C<sub>8</sub>-C<sub>22</sub>fatty alcohol;
- the alkali metal salts, ammonium salts or amine salts of C<sub>8</sub>-C<sub>20</sub>fatty acids, which are termed soaps, typically coconut fatty acid;
- alkylamide sulfates;
- alkylamide ether sulfates;
- alkylaryl polyether sulfates;
- monoglyceride sulfates;

- alkane sulfonates, containing 8 to 20 carbon atoms in the alkyl chain, e.g. dodecyl sulfonate;
- alkylamide sulfonates;
- alkylaryl sulfonates;
- $\alpha$ -olefin sulfonates;
- sulfosuccinic acid derivatives, typically alkyl sulfosuccinates, alkyl ether sulfosuccinates or alkyl sulfosuccinamide derivatives;
- N-[alkylamidoalkyl]amino acids of formula



wherein

X is hydrogen,  $\text{C}_1\text{-C}_4$ alkyl or  $\text{-COO}^-\text{M}^+$ ,

Y is hydrogen or  $\text{C}_1\text{-C}_4$ alkyl,

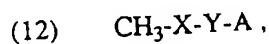
Z is  $\text{-(CH}_2\text{)}_{m_1-1}$ ,

$m_1$  is 1 to 5,

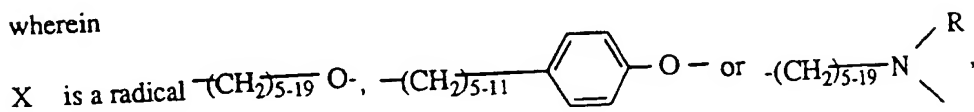
n is an integer from 6 to 18, and

M is an alkali metal ion or an amine ion;

- alkyl ether carboxylates and alkylaryl ether carboxylates of formula



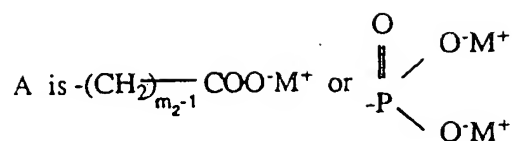
wherein



R is hydrogen or  $\text{C}_1\text{-C}_4$ alkyl,

Y is  $\text{-(CHCHO)}_{1-50}$ ,

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$m_2$  is 1 to 6, and

M is an alkali metal cation or amine cation.

The anionic surfactants used may furthermore be fatty acid methyl taurides, alkylisothionates, fatty acid polypeptide condensates and fatty alcohol phosphoric acid esters. The alkyl radicals in these compounds preferably contain 8 to 24 carbon atoms.

The fatty alcohols which may be present in the above-mentioned surfactants are those containing 8 to 22, preferably 8 to 18 carbon atoms, typically octyl, decyl, lauryl, tridecyl, miristyl, cetyl, stearyl, oleyl, arachidyl or behenyl alcohol.

The anionic surfactants are usually obtained in the form of their water-soluble salts, such as the alkali metal, ammonium or amine salts. Typical examples of such salts are lithium, sodium, potassium, ammonium, triethylamine, ethanolamine, diethanolamine or triethanolamine salts. It is preferred to use the sodium or potassium salts or the ammonium-(NR<sub>1</sub>R<sub>2</sub>R<sub>3</sub>) salts, wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently of one another hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>hydroxyalkyl.

The anionic surfactants preferably used in the formulation of this invention are C<sub>8</sub>-C<sub>22</sub>fatty acid alcohol ether sulfates, more particularly the alkali metal salts of lauryl ether sulfate.

Very particularly preferred anionic surfactants in the novel formulation are monoethanolamine lauryl sulfate or the alkali metal salts of fatty alcohol sulfates, preferably the sodium lauryl sulfate and the reaction product of 2 to 4 mol of ethylene oxide and sodium lauryl ether sulfate.

Suitable zwitterionic and amphoteric surfactants are C<sub>8</sub>-C<sub>18</sub>betaines, C<sub>8</sub>-C<sub>18</sub>sulfobetaines, C<sub>8</sub>-C<sub>24</sub>alkylamido-C<sub>1</sub>-C<sub>4</sub>alkylenebetaines, imidazoline carboxylates, alkylamphocarboxy carboxylic acids, alkylamphocarboxylic acids (e.g. lauroamphoglycinate) and N-alkyl-β-aminopropionates or N-alkyl-β-iminodipropionates. It is preferred to use the C<sub>10</sub>-C<sub>20</sub>alkylamido-C<sub>1</sub>-C<sub>4</sub>alkylenebetaines and, more particularly,

cocoamidopropylbetaine.

Nonionic surfactants are typically derivatives of the adducts of propylene oxide/ethylene oxide having a molecular weight of 1000 to 15000, fatty alcohol ethoxylates (1-50 EO), alkylphenol polyglycol ethers (1-50 EO), ethoxylated carbohydrates, fatty acid glycol partial esters, typically diethylene glycol monstearate, fatty acid alkanolamides and fatty acid dialkanolamides, fatty acid alkanolamide ethoxylates and fatty acid amine oxides. The fatty acid alkanolamides and fatty acid dialkanolamides and, preferably, cocodiethanolamide are to be particularly highlighted.

Suitable components (d) are the salts of saturated and unsaturated C<sub>12</sub>-C<sub>22</sub> fatty acids, typically lauric, myristic, palmitic, stearic, arachic, behenic, dodecenoic, tetradecenoic, octadecenoic, oleic, eicosanic and erucic acid, as well as the technical mixtures of such acids, typically coconut fatty acid which is preferably used in the novel formulation. These acids may be obtained in the form of salts, suitable cations being alkali metal cations such as sodium and potassium cations, metal atoms such as zinc atoms and aluminium atoms or nitrogen-containing organic compounds of sufficient alkalinity, typically amines or ethoxylated amines. These salt can also be prepared in situ. Component (d) can also be a mixture of the indicated salts.

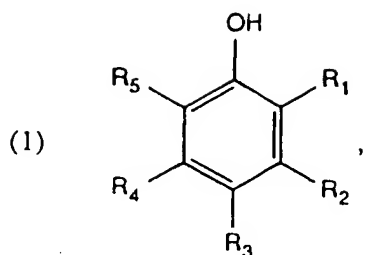
Suitable components (e) are dihydric alcohols, preferably those containing 2 to 6 carbon atoms in the alkylene radical, typically ethylene glycol, 1,2- or 1,3-propanediol, 1,3-, 1,4- or 2,3-butanediol, 1,5-pentanediol and 1,6-hexanediol. 1,2-propanediol (propylene glycol) is preferred.

Component (f) is preferably ethanol, n-propanol and isopropanol or a mixture of these alcohols.

Preferred novel formulations are those comprising

(a<sub>1</sub>) a compound of formula

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wherein

- $R_1$  is hydrogen, hydroxy,  $C_1$ - $C_4$ alkyl, chloro, nitro, phenyl or benzyl,
  - $R_2$  is hydrogen, hydroxy,  $C_1$ - $C_6$ alkyl or chloro,
  - $R_3$  is hydrogen,  $C_1$ - $C_6$ alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,
  - $R_4$  is hydrogen or methyl, and
  - $R_5$  is hydrogen or nitro,
- (b) 0.1 to 25% by weight of a mixture of sodium cumene sulfonate and citric acid monohydrate,
  - (c) 1 to 10% by weight of a  $C_8$ - $C_{22}$ fatty acid alcohol ether sulfate,
  - (e) 0 to 50% by weight of a dihydric alcohol;
  - (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
  - (g) mains water or deionised water to make up 100%.

The pH of the novel formulation is 3 to 10, preferably 4.5 to 6.

The novel formulations obtained as soap or syndet solutions may additionally comprise customary additives, typically sequestrants, dyes, perfume oils, thickeners or solidifiers (consistency regulators), emollients, UV absorbers, skin-protection agents, antioxidants, additives which improve the mechanical properties, such as dicarboxylic acids and/or Al, Zn, Ca, Mg salts of  $C_{14}$ - $C_{22}$ fatty acids and, if desired, preservatives.

The novel soap bars can be fabricated in per se known manner, typically by mixing the novel components (a) and (b) and, optionally, (c), (d), (e) and (f), as well as any additives in a jerk mixer at 18-25°C. After the composition obtained has been processed, it is extruded at 40 to 60°, preferably from 45 to 50°C, and then cut and stamped in moulds.

Soap formulations of the invention can be prepared by mixing components (a) and (b) and, optionally, (c), (d), (e) and (f), in any order, with the requisite amount of water and stirring

the mixture to homogeneity. The mixture is bulked to 100% with additional water. This procedure is a purely physical procedure. Accordingly, there is no chemical reaction of the individual components.

For disinfection and cleansing of the human skin and hands and of hard objects, the novel soap formulations can be applied thereto in dilute or undilute form, suitably in an amount of at least 2 ml, preferably in the undilute form, for hand disinfection.

The invention is illustrated by the following Examples. Parts and percentages are by weight.

Example 1:

1.0 part	o-phenylphenol,
4.0 parts	sodium lauryl ether-2-sulfate,
8.0 parts	sodium cumene sulfonate powder,
8.0 parts	citric acid monohydrate,
10.0 parts	propylene glycol, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 2:

1.0 part	o-phenylphenol,
4.0 parts	sodium lauryl ether-4-sulfate,
8.0 parts	sodium cumene sulfonate powder,
8.0 parts	citric acid monohydrate,
10.0 parts	propylene glycol, and

water to make up 100 parts

is stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 3:

1.0 part            p-chloro-m-xylene,  
4.0 parts          sodium lauryl ether-2-sulfate  
8.0 parts          sodium cumene sulfonate powder,  
8.0 parts          citric acid monohydrate,  
10.0 parts        propylene glycol, and  
water to make up 100 parts

are mixed to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 4:

1.0 part            p-chloro-o-benzylphenol,  
4.0 parts          sodium lauryl ether-2-sulfate  
8.0 parts          sodium cumene sulfonate powder,  
8.0 parts          citric acid monohydrate,  
10.0 parts        propylene glycol, and  
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 5:

2.0 parts          benzyl alcohol,  
4.0 parts          sodium lauryl sulfate  
5.0 parts          sodium cumene sulfonate powder,  
8.0 parts          citric acid monohydrate,  
10.0 parts        propylene glycol, and  
water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 6:

4.0 parts cocamidopropylbetaine,  
5.0 parts sodium cumene sulfonate,  
10.0 parts propylene glycol,  
8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 7:

4.0 parts cocamidopropylbetaine,  
12.0 parts ethanol,  
8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 8:

4.0 parts sodium lauraminopropionate,  
5.0 parts sodium cumene sulfonate,  
10.0 parts propylene glycol,  
8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 9:

4.0 parts sodium lauraminopropionate,  
12.0 parts ethanol,  
8.0 parts citric acid monohydrate, and

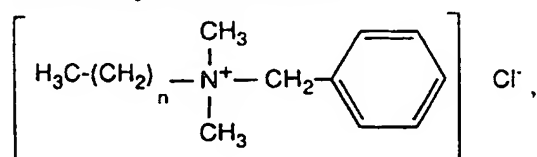


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water to make up 100 parts  
are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 4.0.

Example 10:

1.0 part of the compound of formula



wherein n is an integer from 7 to 17,

4.0 parts cocamidopropylbetaine,

12.0 parts ethanol,

8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 11:

1.0 part 2,4-dichlorobenzyl alcohol

4.0 parts sodium laurylsulfate,

5.0 parts sodium cumene sulfonate,

1.0 part propylene glycol,

8.0 parts citric acid monohydrate, and

water to make up 100 parts

are stirred to homogeneity and about 90% of the requisite water is then added. The pH is adjusted to 5.5 with monoethanolamine. Deionised water is then added to the solution to make up a total of 100 parts. The pH is checked again and, if necessary, monoethanolamine is added to adjust the pH to 5.5.

Example 12: Test of the microbicidal activity of the novel formulations

The microbicidal activity (in decimal logarithms) of the novel formulations according to Examples 1 to 11 is determined with a suspension test. This test is used to assess the bactericidal activity of water-soluble antiseptics, disinfectants and of liquid soaps. The test consists in seeding the test product in selected dilutions with the test bacillus. After a certain contact time, aliquots is taken and the number of surviving bacilli is determined. The difference between the number of the bacilli added and the number of the surviving bacilli is expressed as bacilli reduction in decimal logarithms. The concentration is 90%, the contact time is 30 seconds.

The following test bacilli are used:

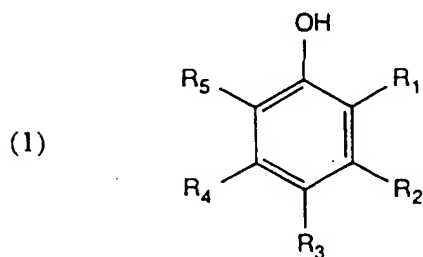
Example	Staph. aureus ATCC 9144	Strept. faecalis ATCC 10,541	E. Coli ATCC 10,536	P.aeruginosa CIP A-22	Serratia mar- cescens ATCC 13,880
1	4.6	>5.1	>5.3	>5.3	>5.4
2	>5.5	>5.2	>5.1	>5.3	>5.5
3	>5.5	>5.2	>5.1	>5.3	>5.5
4	>5.5	>5.2	>5.1	>5.3	>5.5
5	>6	>6	>6	>6	>6
6	2.0	0.2	1.4	>6	2.7
7	0	0.5	2.6	>6	1.3
8	0.1	0.3	0.7	>6	2.5
9	3.5	>6	>6	>6	4.2
10	1.0	1.7	>6	>6	4.7
11	3.4	>6	>6	>6	>6

What is claimed is

## 1. A surface-active surfactant formulation, comprising

- (a) 0.01 to 5% by weight of a microbicidal active substance selected from the group consisting of
- (a<sub>1</sub>) phenol derivatives,
  - (a<sub>2</sub>) diphenyl compounds,
  - (a<sub>3</sub>) benzyl alcohols,
  - (a<sub>4</sub>) chlorohexidine,
  - (a<sub>5</sub>) C<sub>12</sub>-C<sub>14</sub>alkylbetaines and C<sub>8</sub>-C<sub>18</sub>fatty acid amidoalkylbetaines,
  - (a<sub>6</sub>) amphoteric surfactants,
  - (a<sub>7</sub>) trihalocarbanilides, and
  - (a<sub>8</sub>) quaternary ammonium salts;
- (b) 0.1 to 25% by weight of one or more than one hydrotropic agent;
- (c) 0 to 10% by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances;
- (d) 0 to 8% by weight of a salt of a saturated and/or unsaturated C<sub>8</sub>-C<sub>22</sub>fatty acid;
- (e) 0 to 50% by weight of a dihydric alcohol;
- (f) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and
- (g) mains water or deionised water to make up 100%,
- with the proviso that said formulations contain at least one of components (c) and (d).

2. A formulation according to claim 1, wherein the compounds used for component (a<sub>1</sub>) are those of the general formula



wherein

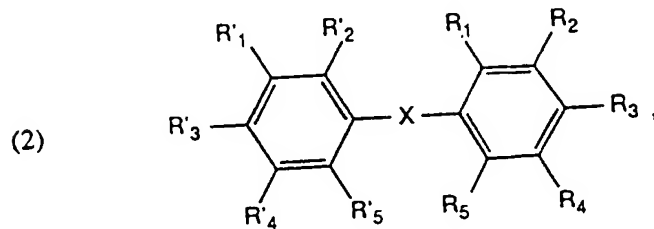
- R<sub>1</sub> is hydrogen, hydroxy, C<sub>1</sub>-C<sub>4</sub>alkyl, chloro, nitro, phenyl oder benzyl,
- R<sub>2</sub> is hydrogen, hydroxy, C<sub>1</sub>-C<sub>6</sub>alkyl or halogen,
- R<sub>3</sub> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the

alkali metal salts or ammonium salts thereof,

$R_4$  is hydrogen or methyl,

$R_5$  is hydrogen or nitro.

3. A formulation according to claim 1, wherein the compounds used for component (a<sub>2</sub>) are those of formula



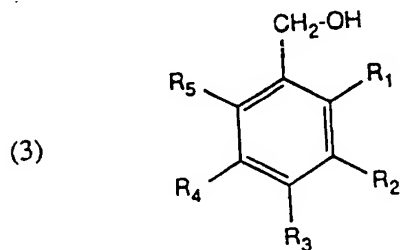
wherein

X is sulfur or the methylene group,

$R_1$  and  $R'_1$  are hydroxy, and

$R_2$ ,  $R'_2$ ,  $R_3$ ,  $R'_3$ ,  $R_4$ ,  $R'_4$ ,  $R_5$  and  $R'_5$  are each independently of one another hydrogen or halogen.

4. A formulation according to claim 1, wherein the compounds used for component (a<sub>3</sub>) are those of formula



wherein

$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  and  $R_5$  are each independently of one another hydrogen or chloro.

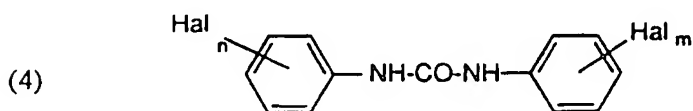
5. A formulation according to claim 1, wherein component (a<sub>4</sub>) is chlorohexidine or a salt thereof with an organic or inorganic acid.

6. A formulation according to claim 1, wherein component (a<sub>5</sub>) is cocamidopropylbetaine.

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7. A formulation according to claim 1, wherein component (a<sub>6</sub>) is a C<sub>12</sub>alkylaminocarboxylic acid or a C<sub>1</sub>-C<sub>3</sub>alkanecarboxylic acid.

8. A formulation according to claim 1, wherein the compounds used for component (a<sub>7</sub>) are those of the general formula



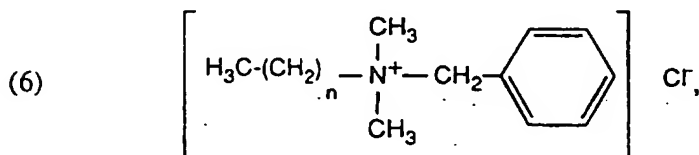
wherein

Hal is chloro or bromo,

n and m are 1 or 2, and

n + m are 3.

9. A formulation according to claim 1, wherein the compound used for component (a<sub>8</sub>) is a compound of formula



wherein

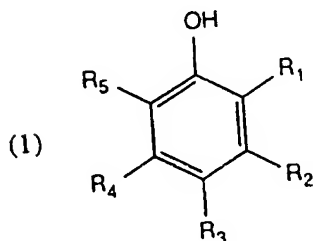
n is an integer from 7 to 17.

10. A formulation according to any one of claims 1 to 9, wherein component (b<sub>1</sub>) is a sulfonate, preferably a salt thereof of a terpenoid or of a mono- or binuclear aromatic compound.

11. A formulation according to claim 10, wherein the mono- or binuclear aromatic compounds are the sulfonates of camphor, toluene, xylene, cumene or naphthene.

12. A formulation according to any one of claims 1 to 11, wherein component (b) consists of only one compound of subclass (b<sub>1</sub>) or also of a mixture of one or more than one compound of subclass (b<sub>1</sub>) together with components of further subclasses.

13. A formulation according to any one of claims 1 to 11, wherein component (b) is a combination of one or more than one compound of subclass (b<sub>1</sub>) and one or more than one compound of subclass (b<sub>2</sub>).
14. A formulation according to claim 13, wherein a combination of cumene sulfonate and citric acid monohydrate is used.
15. A formulation according to any one of claims 1 to 14, wherein component (c) is an anionic surfactant in the form of the water-soluble salt thereof.
16. A formulation according to claim 15, wherein component (c) is C<sub>8</sub>-C<sub>22</sub>fatty alcohol ether sulfate.
17. A formulation according to claim 16, wherein component (c) is an alkali metal salt of lauryl ether sulfate.
18. A formulation according to any one of claims 1 to 17, wherein component (d) is selected from the group consisting of lauric, myristic, palmitic, stearic, arachic, behenic, dodecenic, tetradecenic, octadecenic, oleic, eicosenic and erucic acid.
19. A formulation according to any one of claims 1 to 18, wherein component (e) is propylene glycol.
20. A formulation according to any one of claims 1 to 19, wherein component (f) is selected from the group consisting of ethanol, propanol, isopropanol, and mixtures of these alcohols.
21. A surface-active formulation comprising  
(a<sub>1</sub>) a compound of formula

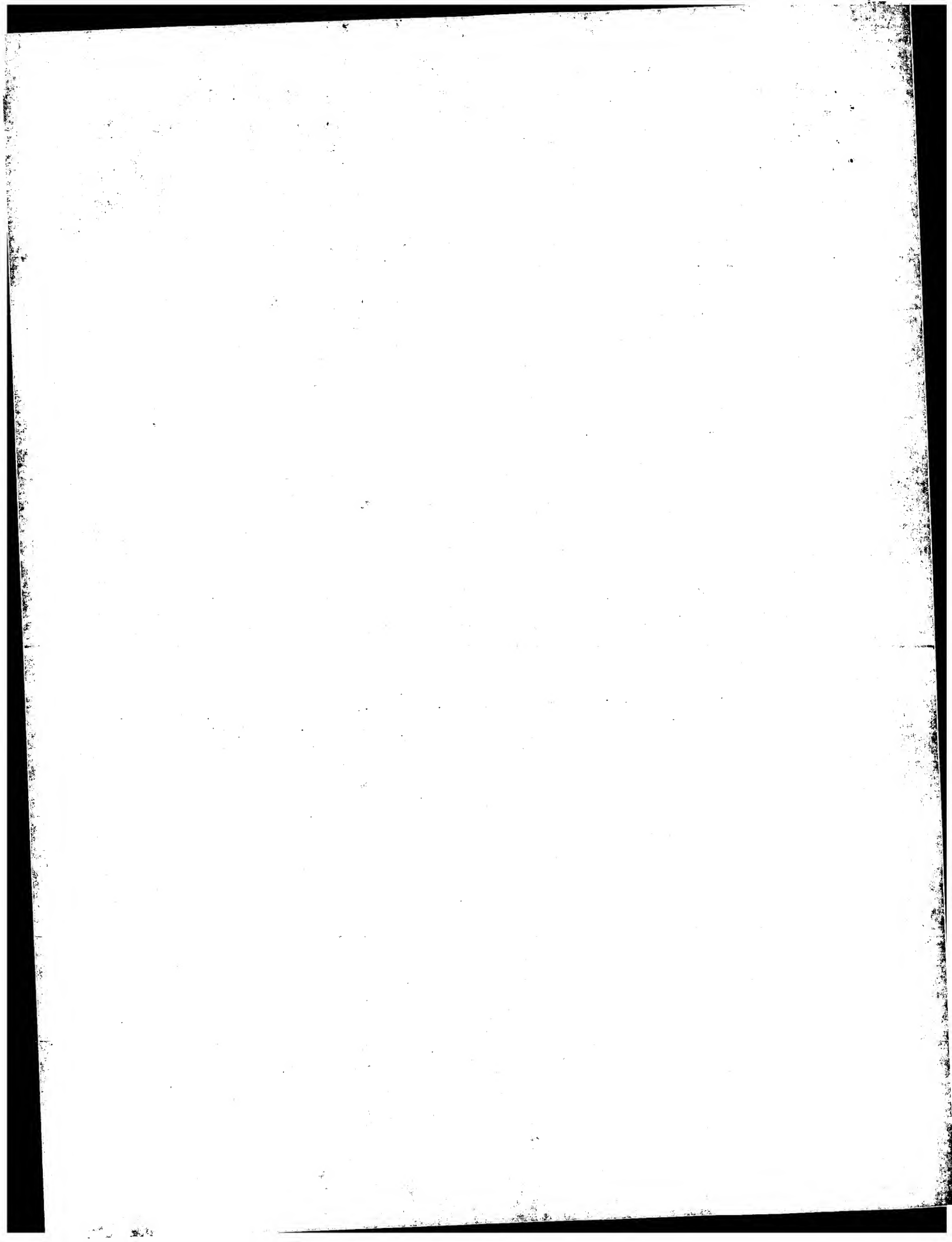


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wherein

- $R_1$  is hydrogen, hydroxy,  $C_1$ - $C_4$ alkyl, chloro, nitro, phenyl oder benzyl,  
 $R_2$  is hydrogen, hydroxy,  $C_1$ - $C_6$ alkyl or halogen,  
 $R_3$  is hydrogen,  $C_1$ - $C_6$ alkyl, hydroxy, chloro, nitro or a sulfo group in the form of the alkali metal salts or ammonium salts thereof,  
 $R_4$  is hydrogen or methyl,  
 $R_5$  is hydrogen or nitro,  
(b) 0.1 to 25% by weight of a mixture of sodium cumene sulfonate and citric acid monohydrate,  
(c) 0 to 10% by weight of a  $C_8$ - $C_{22}$ fatty alcohol ether sulfate,  
(d) 0 to 50% by weight of a dihydric alcohol,  
(e) 0 to 70% by weight of a monohydric alcohol or of a mixture of several monohydric alcohols, and  
(f) mains water or deionised water to make up 100%.

22. Use of an antimicrobial soap formulation as claimed in any one of claims 1 to 21 for the disinfection and cleansing of the human skin and hands and of hard objects.





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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT) (31) International Patent Classification 6 : C11D 3/00, A61K 7/48, 7/50		A3	(11) International Publication Number: WO 96/06153 (43) International Publication Date: 29 February 1996 (29.02.96)
(21) International Application Number: PCT/EP95/03211 (22) International Filing Date: 14 August 1995 (14.08.95) (30) Priority Data: 2611/94-8 25 August 1994 (25.08.94) CH (71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH). (72) Inventor; and (75) Inventor/Applicant (for US only): MOLDOVANYI, Laszlo [CH/CH]; Oberer Batterieweg 15, CH-4059 Basle (CH). (74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. (88) Date of publication of the international search report: 2 May 1996 (02.05.96)	
(54) Title: SURFACE-ACTIVE FORMULATIONS			
(57) Abstract <p>The invention relates to surface-active soap formulations, comprising: (a) 0.01 to 5 % by weight of a microbicidal active substance selected from the group consisting of (a<sub>1</sub>) phenol derivatives (a<sub>2</sub>) diphenyl compounds (a<sub>3</sub>) benzyl alcohols (a<sub>4</sub>) chlorohexidine (a<sub>5</sub>) C<sub>12</sub>-C<sub>14</sub>alkylbetaines and C<sub>8</sub>-C<sub>18</sub>fatty acid amidoalkylbetaines (a<sub>6</sub>) amphoteric surfactants and (a<sub>7</sub>) trihalocarbanilides; (b) 0.1 to 25 % by weight of one or more than one hydrotropic agent; (c) 0 to 10 % by weight of one or more than one synthetic surface-active substance or of a soap or of combinations of the cited substances; (d) 0 to 8 % by weight of a salt of a saturated and/or unsaturated C<sub>8</sub>-C<sub>22</sub>fatty acid; (e) 0 to 50 % by weight of a dihydric alcohol; (f) 0 to 70 % by weight of a monohydric alcohol or of a mixture of several monohydric alcohols; and (g) mains water or deionised water to make up 100 %, with the proviso that the formulations contain at least one of components (c) and (d). The formulations are used for the disinfection and cleansing of the human skin and hands and of hard objects.</p>			

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 95/03211

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C11D3/00 A61K7/48 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,37 23 990 (CIBA-GEIGY AG.) 4 February 1988  see the whole document ---	1,3,6, 15-17, 19,20,22
X	CH,A,552 670 (UNILEVER PLC) 15 August 1974 see the whole document ---	1,3,8,22
X	GB,A,1 408 885 (CIBA-GEIGY AG.) 8 October 1975  see the whole document ---	1,3,10, 11,15, 16,20,22
X	FR,A,1 501 612 (HENKEL KOMMANDIT GESELLSCHAFT AUF AKTIEN) 31 January 1968  see the whole document ---	1-3,8, 10,11, 15,16, 20,22
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 February 1996

Date of mailing of the international search report

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NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
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# INTERNATIONAL SEARCH REPORT

Inventor's Application No  
PCT/EP 95/03211

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim No.
Category *	Citation of document, with indication, where appropriate, of the relevant passages	
X	<p>DATABASE WPI Week 8941 Derwent Publications Ltd., London, GB; AN 89-292819 &amp; AU,A,3 001 889 (CIBA-GEIGY AG.) , 17 August 1989 see abstract</p>	1,3,22
X	<p>--- DE,A,31 17 792 (SCHÜLKE &amp; MAYR GMBH) 18 November 1982 see the whole document</p>	1-3,9, 20-22
X	<p>--- FR,A,2 301 233 (BEECHAM GROUP LIMITED) 17 September 1976 see the whole document</p>	1-3,9, 20-22
X	<p>--- EP,A,0 433 911 (KAO CORPORATION) 26 June 1991 see the whole document</p>	1-3,8,9, 19-22
X	<p>--- DE,A,37 23 994 (CIBA-GEIGY AG.) 4 February 1988 see the whole document</p>	1,3,15, 16,20,22
X	<p>--- DATABASE WPI Week 9347 Derwent Publications Ltd., London, GB; AN 93-374809 &amp; JP,A,05 279 693 (SHINETSU CHEM IND CO LTD) , 26 October 1992 see abstract</p>	1,3,22
X	<p>--- EP,A,0 047 033 (THE PROCTER &amp; GAMBLE COMPANY) 10 March 1982 see the whole document</p>	1,8,22
A	<p>--- US,A,4 832 861 (RESCH) 23 May 1989 see the whole document</p>	1-6,15, 19,20
A	<p>--- DE,A,22 61 030 (BASF WYANDOTTE CORP.) 20 December 1972 see the whole document</p>	1,22
A	<p>--- DATABASE WPI Week 8829 Derwent Publications Ltd., London, GB; AN 88-202120 &amp; JP,A,63 139 998 (LION CORP.) , 11 June 1988 see abstract</p>	1,3,8,22
A	<p>--- WO,A,94 10837 (WEST AGRO INC.) 26 May 1994 see the whole document</p>	1,22

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 95/03211

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